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④ Use of a negative acting photopolymerizable element as a solder mask.

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EP-A-0 049 504
FR-A-1 381 607
FR-A-2 074 487
FR-A-2 316 625
GB-A-2 062 647

RESEARCH DISCLOSURE, no. 104, December
1972, pages 53-54, no. 10449, Havant, Hants.,
GB "Photopolymerizable compositions and
elements containing organosilanes"

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Courier Press, Leamington Spa, England.

Description

This invention relates to the use of a photopolymerizable element as a solder mask and more particularly to the use of such film in which improved release properties can be obtained.

U.S. Patent 3,469,982 discloses a negative acting photopolymerizable film resist in which a photopolymerizable layer is sandwiched between a temporary support film and a temporary cover film. This film has gained widespread usage of the manufacture of printed circuits in which the cover film is removed, the photopolymerizable layer is laminated by heat and pressure to the surface, e.g., copper, of a substrate to be permanently modified, the layer is imagewise exposed to actinic radiation, the film support is removed, the unexposed areas of the layer are removed by solvent washout (development), and the resultant bared area of the copper surface is permanently modified, such as by etching or deposition of metal.

The patent discloses solution coating of a photopolymerizable composition onto the support film, followed by drying and then lamination of the resultant dry layer to a surface such as copper-clad printed circuit board to carry out the photoresist process. In commercial practice, however, the dried photopolymerizable layer, which must remain adhered to the support during storage and shipment, has always been supplied as a sandwich between the support film and a cover sheet. This has enabled the sandwich element to be rolled up upon itself by the photoresist manufacturer and be supplied to the user, e.g., printed circuit manufacturer, as a compact, easy to handle roll. The cover film permits the roll to be unrolled by the user without the cover film pressing the prior art photopolymerizable layer against the backside of the support film and causing that layer to adhere. Consequently, the film could not be unrolled without damaging the photopolymerizable layer. In use, the cover film is stripped away and discharged, followed by the photoresist processing described above.

This type of photopolymerizable film sandwiched between a temporary support film and a temporary cover film can be formulated to be useful in solder mask applications wherein the photopolymerizable film is applied to portions of a printed circuit board surface to confine molten solder heated to a temperature of at least 230°C to pad areas on the board and to prevent bridging between conductors during tinning operations and during soldering of components. A solder mask also functions to prevent or minimize corrosion of the bare copper conductors and as a dielectric to insulate certain components from adjacent circuitry. Since a solder mask remains on the finished circuit board, i.e., the solder mask is a permanent coating for the printed circuit, it usually is transparent to allow for ease of circuit inspection.

Prior to use of the photopolymerizable layer it is necessary to remove the cover sheet to allow the photopolymerizable layer to be applied to a substrate which may or may not contain circuitry.

The present invention is directed to the introduction of an additive into a negative acting photosensitive composition which will allow easier removal of the cover sheet.

Use of additives in photosensitive layers is known in the prior art. Additives useful in the present invention are known in U.S.—A—3,827,908 to improve adhesion of positive photoresist to oxide semiconductor surfaces.

EP—A—0,049,504, which document falls within the terms of Art. 54(3) EPC, is concerned with the preparation of dry photoresists having improved developability rates. These photoresists may have the same composition as the photopolymerizable elements used in the present invention. The photoresists are circuit boards for making multilayer photocircuits. FR—A—1,381,607 discloses a photopolymerizable composition containing an ethylenically unsaturated compound, an aqueous dispersion of a polymerizable, a tensioactive agent and a polymerization initiator. The tensioactive agent may be disodium N-alkyl-β-iminodipropionate, in which the alkyl group contains from the 14 to 18 carbon atoms. The photoresists are applied to a substrate and may be protected by a cover sheet.

Summary of the invention

The present invention is directed to the use of a solvent-developable negative acting radiation sensitive photopolymerizable element as a solder mask said element comprising a support bearing a layer of negative acting photopolymerizable composition, useful in making printed circuits, and a cover sheet with said composition comprising:

- (a) at least one addition polymerizable ethylenically unsaturated compound having a boiling point above 100°C at normal pressure;
 - (b) an organic free radical-generating addition polymerization initiator activatable by actinic radiation in the ultraviolet-to-visible region of the spectrum and
 - (c) a macromolecular organic polymeric binder which comprises a release compound or mixture of the formula A—B wherein:
- 60 A is substituted or unsubstituted alkyl or alkenyl of 6 to 24 carbon atoms, and
 B is a 5 or 6 atom aromatic or nonaromatic heterocyclic radical containing 2 or 3 hetero atoms taken from N, O, S or combination thereof, said radical optionally containing a six carbon fused aromatic ring, or B is an alkali metal salt of a β-aminocarboxylic acid or a bis alkali metal salt of a β, β'-aminodicarboxylic acid, wherein said release compound or mixture is present in said negative acting photopolymerizable composition in an effective amount sufficient to lower peel force to a value not greater than 29 N/m.

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Detailed description of the invention

The introduction of an additive into the negative acting solvent developable radiation sensitive composition aids in removal of the cover sheet which protects the radiation sensitive composition, e.g., in storage. This additive is of the formula A—B wherein A—B is as previously defined.

5 A narrow class of A—B groups are where

A is a straight chain alkyl or straight chain alkenyl of 6 to 24 carbon atoms,

B is 1-hydroxyethyl-2-imidazoliny, sodium propion-2-yl-amino, or bis-(sodium propion-2-yl)-imino.

10 Preferred A—B constituents are where A contains 6 to 18 carbon atoms and B is 1-hydroxyethyl-2-imidazoliny. Examples of suitable compounds are where A is octyl, 9-octadecanyl, alkyl derived from tall oil fatty acid, or, alkyl derived from coconut oil fatty acid and B is 1-hydroxyethyl-2-imidazoliny. Examples of compounds for other A—B constituents are where A is alkyl derived from coconut oil fatty acid and B is sodium propion-2-yl-amino and A is alkyl derived from tallow and B is bis-(sodium propion-2-yl)-imino.

15 Additional compounds within the scope of the present invention are those having the heterocyclic group B of

4-pyrazolyl-

1,2,4-triazolyl-3-

20 4-oxazolyl-

1,3,4-thiadiazolyl-2-

3-benzotriazolyl-

2-pyrazinyl-.

25 The release compounds above are present in an amount effective to result in a peel force not greater than 29 N/m and preferably not greater than 9.7 N/m. "Peel force" is measured in accordance with the procedure listed below in the section entitled "Testing Procedure". The compound or mixture of compounds is generally present in an amount of 1 to 10% by weight based on the total weight of the negative acting photopolymerizable composition. A more preferred range is 1 to 5% by weight and more preferably 2 to 4%.

30 The photopolymerizable compositions as described above are limited only in that the components must be compatible with one another, and they must be capable of being formed into dry layers. A preferred photosensitive composition except for the release additive is disclosed in U.S.—A—4,278,752. This patent discloses a preferred photopolymerizable composition which comprises: (a) up to four ethylenically

35 unsaturated compounds, preferably two or three, 20 to 65% by weight; (b) up to three macromolecular organic polymeric binders, preferably two, 20 to 35% by weight, at least one binder containing at least 5% by weight acrylonitrile; and (c) an organic, free-radical generating addition polymerization initiator or initiator system activatable by actinic radiation in the ultraviolet to visible region of the spectrum, 0.4 to 10.0% by weight, the composition containing at least 5% by weight halogen, e.g., bromine, chlorine,

40 covalently bonded to an aromatic moiety or a conjugated vinyl component. All the weight percentages are based on the total weight of the composition. Covalent bonded halogen is desirable if the composition is to be used for soldering applications so that the layer can withstand soldering without blistering or degradation as occurs when the halogen is not covalently bonded to one of the aforesaid components. Effective components are those wherein the halogen is covalently bonded to an aromatic moiety of at least

45 one of the ethylenically unsaturated compound (a), polymeric binder (b) and initiator (c), or to at least one conjugated vinyl component, e.g., in either monomeric form or as a polymer such as 2-chlorobutadiene-1,3. Effective compounds are therefore aryl halides and conjugated vinyl halides. Compounds such as vinylidene chloride copolymers, e.g., vinylidene chloride/acrylonitrile copolymers, are undesirable for soldering applications because they are saturated compounds which lose hydrogen chloride upon heating.

50 The presence of such compounds in the solder mask results in blistering or degradation of the solder mask.

The halogen can be present in the composition covalently bonded to one, two or three of the components described above or any combination thereof, many of which are illustrated in the examples of U.S.—A—4,278,752. In a particularly preferred composition, 10 to 50% by weight of the ethylenically unsaturated compounds are halogenated. At the lower level of halogen present in the composition up to 10% by weight of Sb₂O₃ can be present to further increase flame retardance in solder mask applications.

55 Above the 10% by weight amount the desirable properties of the photopolymerizable element, e.g., adhesion, surface smoothness etc., begin to degrade. As the amount of halogen in the composition increases, the quantity of Sb₂O₃ can be reduced or eliminated entirely.

The preferred radiation sensitive element comprises a photopolymerizable layer with a thickness of about 8 µm (0.0003 inch) to about 250 µm (0.01 inch) having adhered thereto with low to moderate adherence a thin, flexible polymeric film support which transmits radiation actinic to the photopolymerizable layer. The other side of the photopolymerizable layer may have adhered thereto a protective cover sheet with less adherence to the layer than adherence between the support and the layer.

60 A suitable cover sheet which is removable prior to application of the radiation sensitive material to a substrate may be chosen from a wide variety of films composed of high polymers, e.g., polyamides,

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polyolefins, polyesters, vinyl polymers, and cellulose esters, and may have a thickness of from 6 μm (0.00025 inch) to 200 μm (0.008 inch) or more. A preferred cover sheet is about 25 μm (0.01 inch) thick polyethylene. Cover sheets and their compositions are well known in the prior art.

- A suitable support sheet may be chosen from the same group of high polymer films described above and may have the same wide range of thicknesses. If exposure is to be made before removing the strippable support, it must, of course, transmit a substantial fraction of the actinic radiation incident upon it. If the strippable support is removed prior to exposure, no such restrictions apply. A particularly suitable support is a transparent polyethylene terephthalate film having a thickness of about 25 μm (0.001 inch). Supports and cover sheets as described above provide good protection to the photopolymerizable layer.
- 10 The flexible, photopolymerizable layer is prepared from monomeric components, polymeric binder components, photopolymerization initiators and other additives set forth below. It is preferable that at least a minimum amount of halogen is present and the binder preferably contains acrylonitrile to provide flexibility to the layer even after photoexposure and exposure to molten solder. A desirable range of acrylonitrile is 5 to 15%.
- 15 Suitable monomers having a boiling point greater than 100°C at normal pressure which can be used as the sole manner or in combination with others include the following: tribromophenoxy ethyl methacrylate, 1,5-pentanediol diacrylate, ethylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-propanediol diacrylate, dicarnethylene glycol diacrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylolpropane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, 2,2-di(p-hydroxyphenyl)propane diacrylate, pentaerythritol tetraacrylate, 2,2-di(p-hydroxyphenyl)propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2,2-di(p-hydroxyphenyl)propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl)ether of bisphenol-A, di-(2-methacryloxyethyl)ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl)ether of bisphenol-A, di-(2-acryloxyethyl)ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl)ether of tetrachloro bisphenol-A, di(2-methacryloxyethyl)ether of tetrachloro bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl)ether of tetrabromo bisphenol-A, di-(2-methacryloxyethyl)ether of tetrabromo bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl)ether of 1,4-butanediol, di-(3-methacryloxy-2-hydroxypropyl)ether of diphenolic acid, triethylene glycol dimethacrylate, polyoxypropyltrimethylol propane triacrylate, ethylene glycol trimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 2,2,4-trimethyl-1,3-pantanediol dimethacrylate, pentaerythritol trimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,5-pantanediol dimethacrylate, dialyl fumarate, 1,4-benzenediol dimethacrylate, 1,4-diisopropenyl benzene, and 1,3,5-triisopropenyl benzene.
- 35 Also useful in the photopolymerizable layer is at least one of the following ethylenically unsaturated compounds having a molecular weight of at least 300. Preferred monomers of this type are: an alkylene or a polyalkylene glycol diacrylate prepared from an alkylene glycol of 2 to 15 carbons or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in U.S. Patent 2,927,022, e.g., those having a plurality of addition polymerizable ethylenic linkages particularly when present as terminal linkages and especially 40 those wherein at least one and preferably most of such linkages are conjugated with a double bonded carbon, including carbon doubly bonded to carbon and to such heteroatoms as nitrogen, oxygen and sulfur. Outstanding are such materials wherein the ethylenically unsaturated groups, especially the vinylidene groups, are conjugated with ester or amide structures.
- Suitable binders which can be used as the sole binder or in combination with others include the following: Polyacrylate and alpha-alkyl polyacrylate esters, e.g., polymethyl methacrylate and polyethyl methacrylate; polyvinyl esters, e.g., polyvinyl acetate, polyvinyl acetate/acrylate, polyvinyl acetate/methacrylate and hydrolyzed polyvinyl acetate, ethylene/vinyl acetate copolymers; polystyrene polymers and copolymers, e.g., with maleic anhydride and esters, saturated and unsaturated polyurethanes; synthetic rubbers, e.g., butadiene/acrylonitrile, acrylonitrile/butadiene/styrene and/or bromostyrene, 50 methyl methacrylate/acrylonitrile/butadiene/styrene copolymers, 2-chlorobutadiene/1,3-polymers, and styrene/butadiene/styrene, styrene/isoprene/styrene block copolymers; polybromostyrene; polyethylene oxides of polyglycols having average molecular weights from about 4,000 to 1,000,000; epoxides, e.g., epoxides containing acrylate or methacrylate groups; copolyesters, e.g., those prepared from the reaction product of a polymethylene glycol of the formula HO(CH₂)_nOH, where n is a whole number 2 to 10 inclusive, 55 and (1) hexahydroterephthalic, sebacic and terephthalic acids, (2) terephthalic, isophthalic and sebacic acids, (3) terephthalic and sebacic acids, (4) terephthalic and isophthalic acids, and (5) mixtures of copolymers prepared from said glycols and (i) terephthalic, isophthalic and sebacic acids and (ii) terephthalic, isophthalic, sebacic and adipic acids; nylons or polyamides, e.g., N-methoxymethyl polyhexamethylene adipamide; cellulose esters, e.g., cellulose acetate, cellulose acetate succinate and 60 cellulose acetate butyrate; cellulose ethers, e.g., methyl cellulose, ethyl cellulose and benzyl cellulose; polycarbonates; polyvinyl acetal, e.g., polyvinyl butyral, polyvinyl formal; polyformaldehyde.
- Preferred free-radical generating addition polymerization initiators activatable by actinic light and thermally inactive at and below 185°C include the substituted or unsubstituted polynuclear quinones which are compounds having two intracyclic carbon atoms in a conjugated carbocyclic ring system, e.g., 65 9,10-anthraquinone, 1-chloroanthraquinone, 2-chloroanthraquinone, 2-methyl-anthraquinone, 2-

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- ethylanthraquinone, 2-tert-butylanthraquinone, octamethylanthraquinone, 1,4-naphthoquinone, 9,10-phenanthrenequinone, 1,2-benzanthraquinone, 2,3-benzanthraquinone, 2-methyl-1,4-naphthoquinone, 2,3-dichloronaphthoquinone, 1,4-dimethylanthraquinone, 2,3-dimethylanthraquinone, 2-phenylanthraquinone, 2,3-diphenylanthraquinone, sodium salt of anthraquinone alpha-sulfonic acid, 3-chloro-2-methylanthraquinone, retenequinone, 7,8,9,10-tetrahydro naphthacenequinone, and 1,2,3,4-tetrahydrobenz(a)anthracene-7,12-dione. Other photoinitiators which are also useful, even though some may be thermally active at temperatures as low as 85°C, are described in U.S. Patent 2,760,863 and include vicinal ketaldonyl alcohols, such as benzoin, pivaloin, acryloin ethers, e.g., benzoin methyl and ethyl ethers; α-hydrocarbon substituted aromatic acyloins, including α-methylbenzoin, α-allylbenzoin and α-phenylbenzoin. Photoreducible dyes and reducing agents disclosed in U.S. Patents 2,850,445; 2,875,047; 3,097,096; 3,074,974; 3,097,097; and 3,145,104 as well as dyes of the phenazine, oxazine, and quinone classes; Michler's ketone, benzophenone, 2,4,5-triphenylimidazolyl dimers, e.g., 2-o-chlorophenyl-4,5-diphenylimidazolyl dimer, with hydrogen donors, and mixtures thereof as described in U.S. Patents 3,427,161; 3,479,185 and 3,549,367, can be used as initiators.
- 15 Other useful additives include thermal inhibitors, colorants, plasticizers, fillers, etc. Some of the ingredients can act as a dual role. For example, in the monomer binder systems the ethylenically unsaturated photopolymerizable compound can also act as a plasticizer for the thermoplastic binder. Thermal polymerization inhibitors that can be used in photopolymerizable compositions are: p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6-di-tert-butyl-p-cresol, phenothiazine, pyridine, nitroso dimers, e.g., 1,4,4-trimethyl-2,3-diazobicyclo[3.2.2]-non-ene-2,3-dioxide nitrobenzene and dinitrobenzene, p-toluquinone and chloranil.
- 20 Various dyes and pigments may be added to increase the visibility of the solder-resist image. Any colorant used, however, should preferably be transparent to the actinic radiation used.
- 25 As discussed above, preferred composition of radiation-sensitive photopolymerizable elements are especially useful as solder masks. They are particularly advantageous because they possess resistance to molten solder and flame retardance without the sacrifice of other properties, e.g., flexibility after exposure, adhesion, photospeed, electrical insulation, and moisture, heat, and solvent resistance needed for resist and solder mask functionality as a solder resist and permanent coating for printed circuits.
- 30 The negative acting radiation sensitive photopolymerizable compositions are solvent developable or processable as opposed to semi-aqueous or aqueous developable or processable composition.
- 35 The following example, wherein the weights are in percent unless otherwise indicated, illustrate the invention.

Example

Test films were prepared using the following stock solution:

	Ingredient	Amount (gms)
40	Methylene Chloride	203.0
	Epocryl® 303 Resin di(3-acryloxy-2-hydroxypropyl) ether of tetrabromo bisphanol-A	24.9
45	Pentaerythritol Triacrylate	13.4
	Blendex® 491 methyl methacrylate(46)/acrylonitrile (9)/butadiene(14)/styrene(31) resin	32.6
50	Lucite® 147KNL methyl methacrylate(95)/ethyl methacrylate(5) copolymer	9.0
	CP 19Y methyl methacrylate(92)/methacrylic acid (8)	1.2
55	Benzophenone	6.0
	Michler's ketone	0.5
	3-Mercaptotriazole	0.2
60	RMP-25 Monastral® green pigment (25 parts); methyl methacrylate (46)/ acrylonitrile(9)/butadiene(14)/ styrene(31) resin (75 parts)	0.7

Various amounts of different release agents were added to the stock solution composition above. The solutions were then coated onto 0.0025 cm polyethylene terephthalate film with a 0.038 cm doctor knife. The film was allowed to air dry and a 0.0025 cm polyethylene cover sheet was laminated on the coating.

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Testing procedure:

Films prepared as above were cut into strips 2.54 cm by 25.4 cm. The polyethylene cover sheet was partially lifted from the coating at one end. The polyethyl n terephthalate film with coating was placed in the jaws of a properly calibrated Instr n® device and the polyethyl ne c ver sheet was attached to the other jaw. The load required to remove the rest of the polyethylene from the coating was measured. In a similar manner, the load to remove the polyethylene terephthalate film could be measured by completely removing the polyethylene cover sheet from the strip and not roll laminating the coating to a 5.08 cm by 25.4 cm copper panel. The polyethylene terephthalate film was partially lifted from the coating at one end and the copper board with coating was placed in the jaws of the Instron® device. The polyethylene terephthalate film was attached to the other jaw and the load to remove the rest of the polyethylene terephthalate was measured. This load is equivalent to peel force employed supra.

The following are data obtained for different amounts of Monazoline® CY additive:

15	Amount of Monazoline® CY (wt%)	Load to remove polyethylene (gms)	Load to remove polyethylene terephthalate (gms)
20	0	106	greater than 500
	.5	94	greater than 500
	1.0	76	greater than 500
25	2.0	26	67
	4.0	5	8

By using this procedure, the following compounds were effective at improving the cover sheet release:

30	Compound	Structure
35	Monazoline® CY	A=Octyl
	Monazoline® T	A=Alkyl from tall oil fatty acid
	Monazoline® O	A=9-octadecenyl
	Monazoline® C	A=Alkyl from coconut oil fatty acid
B for the four compounds above is 1-hydroxyethyl-2-imidazolinyl		
40	Deriphat® 151	B=—NHCH ₂ CH ₂ COO [⊖] Na [⊕] A=Alkyl from coconut oil fatty acids CH ₂ CH ₂ COO [⊖] Na [⊕]
45	Deriphat® 154	B=N CH ₂ CH ₂ COO [⊖] Na [⊕]
A=Alkyl from tallow		

50 Claims

1. Use of a solvent-developable negative acting radiation sensitive photopolymerizable element as a solder mask said element comprising a support bearing a layer of negative acting photopolymerizable composition, useful in making printed circuits, and a cover sheet with said composition comprising:
 - (a) at least one addition polymerizable ethylenically unsaturated compound having a boiling point above 100°C at normal pressure;
 - (b) an organic free radical-generating addition polymerization initiator activatable by actinic radiation in the ultraviolet-to-visible region of the spectrum and
 - (c) a macromolecular organic polymeric binder which comprises a release compound or mixture of the formula A—B wherein A is substituted or unsubstituted alkyl or alkenyl of 6 to 24 carbons at most, and B is a 5 or 6 atom aromatic or nonaromatic heterocyclic radical containing 2 or 3 hetero atoms taken from N, O, S or combinations thereof, said radical optionally containing a six carbon fused aromatic ring, or B

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is an alkali metal salt of a β -amino carboxylic acid or a bis alkali metal salt of a β , β' -amino dicarboxylic acid, wherein said release compound or mixture is present in said negative acting photopolymerizable composition in an effective amount sufficient to lower peel force to a value not greater than 29 N/m.

5 2. Use of the element according to claim 1 wherein:

A is a straight chain alkyl or straight chain alkenyl of 6 to 24 carbon atoms
B is 1-hydroethyl-2-imidazolinyl, sodium propion-2-yl-amino, or bis-(sodium propion-2-yl)-imino.

- 10 3. Use of the element according to claims 1 or 2 wherein A contains 6 to 8 carbon atoms.
4. Use of the element according to claims 1 or 2 wherein B is 1-hydroxyethyl-2-imidazolinyl.
5. Use of the element according to claims 1 or 2 wherein A is octyl, 9-octadecenyl, alkyl derived from tall oil fatty acid, or alkyl derived from coconut oil fatty acid.
6. Use of the element according to claim 1 wherein B is 1-hydroxyethyl-2-imidazolinyl-sodium propion-2-yl-amino or bis-(sodium propion-2-yl)-imino.
15 7. Use of the element according to claims 1 or 2 wherein said release compound or mixture is present in said negative acting photopolymerizable composition in an amount of 1 to 10% by weight.
8. Use of the element according to claim 7 wherein said release compound or mixture is present in an amount of 1 to 5% by weight.
20 9. Use of the element according to claim 8 wherein said release compound or mixture is present in an amount of 2 to 4% by weight.

Patentansprüche

25 1. Verwendung eines mit Lösungsmittel entwickelbaren, negativ arbeitenden, strahlungsempfindlichen photopolymerisierbaren Elements als Lötmasse, wobei dieses Element einen Träger umfaßt, der eine bei der Herstellung gedruckter Schaltungen nutzbare Schicht aus einer negativ arbeitenden photopolymerisierbaren Zusammensetzung und eine Deckfolie trägt, wobei die genannte Zusammensetzung umfaßt:

- 30 (a) wenigstens eine additionspolymerisierbare, ethylenisch ungesättigte Verbindung mit einem Siedepunkt über 100°C bei normalem Druck;
(b) einen organischen, freie Radikale erzeugenden Additionspolymerisations-Initiator, der durch aktinische Strahlung im ultravioletten bis sichtbaren Bereich des Spektrums aktivierbar ist,
35 (c) ein makromolekulares organisches polymeres Bindemittel, das eine Trenn-Verbindung oder -Mischung der Formel A—B enthält, worin
A ein substituiertes oder unsubstituiertes Alkyl oder Alkenyl mit 6 bis 24 Kohlenstoff-Atomen ist und
B ein 5 oder 6 Atome umfassender, aromatischer oder nicht-aromatischer heterocyclischer Rest, der 2 oder 3 Hetero-Atome ausgewählt aus N, O, S oder deren Kombinationen enthält, wobei der Rest gegebenenfalls einen anellierten Sechs-Kohlenstoff-Ring enthält, oder
40 B ein Alkalimetall-Salz einer β -Aminocarbonsäure oder ein Bis-Alkalimetall-Salz einer β,β' -Amino-dicarbonsäure ist,
wobei die Trenn-Verbindung oder -Mischung in der negativ arbeitenden photopolymerisierbaren Zusammensetzung in einer Wirkamen Menge vorhanden ist, die ausreicht, um die Abhebekraft auf einen Wert von nicht mehr als 29 N/m zu erniedrigen.

45 2. Verwendung des Elements nach Anspruch 1, worin

A ein geradkettiges Alkyl oder ein geradkettiges Alkenyl mit 6 bis 24 Kohlenstoff-Atomen ist und
50 B 1-Hydroxyethyl-2-imidazolinyl, Natrium-propion-2-ylamino oder Bis-(Natrium-propion-2-yl)imino ist.

3. Verwendung des Elements nach Ansprüchen 1 oder 2, worin A 6 bis 8 Kohlenstoff-Atome enthält.
4. Verwendung des Elements nach Ansprüchen 1 oder 2, worin B 1-Hydroxyethyl-2-imidazolinyl ist.
5. Verwendung des Elements nach Ansprüchen 1 oder 2, worin A Octyl, 9-Octadecenyl, von
55 Tallöl-Fettsäure abgeleitetes Alkyl oder von Kokosnuß-Fettsäure abgeleitetes Alkyl ist.
6. Verwendung des Elements nach Anspruch 1, worin B 1-Hydroxyethyl-2-imidazolinyl, Natrium-propion-2-yl-amino oder Bis-(Natrium-propion-2-yl)imino ist.
7. Verwendung des Elements nach Ansprüchen 1 oder 2, worin die Trenn-Verbindung oder -Mischung
60 in der negativ arbeitenden photopolymerisierbaren Zusammensetzung in einer Menge von 1 bis 10 Gew.-% vorhanden ist.
8. Verwendung des Elements nach Anspruch 7, worin die Trenn-Verbindung oder -Mischung in einer Menge von 1 bis 5 Gew.-% vorhanden ist.
9. Verwendung des Elements nach Anspruch 7, w
65 rin die Trenn-Verbindung oder -Mischung in einer Menge von 2 bis 4 Gew.-% vorhanden ist.

Revendications

1. Utilisation comme masque à soudure d'un élément polymérisable, sensible à un rayonnement, travaillant en négatif, développable par un support portant une couche de composition photopolymérisable travaillant en négatif, utile dans la fabrication de circuits imprimés, et une feuille de couverture, ladite composition comprenant:
- (a) au moins un composé éthyéniquement insaturé polymérisable par addition, ayant un point d'ébullition supérieur à 100°C à la pression normale;
 - (b) un initiateur organique de polymérisation par addition engendrant des radicaux libres, activable par un rayonnement actinique de la région ultraviolette à visible du spectre; et
 - (c) un liant polymère organique macromoléculaire, qui comprend un composé ou mélange anti-adhérence de la formule A—B dans laquelle
- A est un groupe alkyle ou alcényle substitué ou non substitué de 6 à 24 atomes de carbone, et
- B est un radical hétérocyclique aromatique ou non aromatique à 5 ou 6 atomes contenant 2 ou 3 hétéroatomes choisis parmi N, O, S ou une combinaison de ceux-ci, ledit radical contenant éventuellement un noyau aromatique condensé à six atomes de carbone, ou bien B est un sel de métal alcalin d'un acide β-amino-carboxylique ou un sel de bis(métal alcalin) d'un acide β,β'-amino-dicarboxylique, ledit composé ou mélange anti-adhérence étant présent dans ladite composition photopolymérisable travaillant en négatif en une proportion efficace suffisante pour abaisser la force de décollement à une valeur non supérieure à 29 N/m.
2. Utilisation de l'élément selon la revendication 1, dans lequel
- A est un groupe alkyle à chaîne droite ou alcényle à chaîne droite de 6 à 24 atomes de carbone, B est un radical 1-hydroxyéthyl-2-imidazolinyle, sodium-propion-2-yl-amino ou bis(sodium-propion-2-yl)imino.
3. Utilisation de l'élément selon la revendication 1 ou 2, dans lequel A contient 6 à 8 atomes de carbone.
4. Utilisation de l'élément selon la revendication 1 ou 2, dans lequel B est un radical 1-hydroxyéthyl-2-imidazolinyle.
5. Utilisation de l'élément selon la revendication 1 ou 2, dans lequel A est un groupe octyle, 9-octadécényle, alkyle dérivé d'acide gras de tallol ou alkyle dérivé d'acide gras d'huile de coprah.
6. Utilisation de l'élément selon la revendication 1, dans lequel B est un radical 1-hydroxyéthyl-2-imidazolinyle, sodium-propion-2-yl-amino ou bis(sodium-propion-2-yl)imino.
7. Utilisation de l'élément selon la revendication 1 ou 2, dans lequel ledit composé ou mélange anti-adhérence est présent dans ladite composition photopolymérisable travaillant en négatif en une proportion de 1 à 10% en poids.
8. Utilisation de l'élément selon la revendication 7, dans lequel ledit composé ou mélange anti-adhérence est présent en une proportion de 1 à 5% en poids.
9. Utilisation de l'élément selon la revendication 8, dans lequel ledit composé ou mélange anti-adhérence est présent en une proportion de 2 à 4% en poids.

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